III.B.5 Diesel Fuel Reforming Kinetics

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Objectives

- Provide kinetic reaction rate and process information of diesel fuel reforming to support the development of auxiliary power units (APUs) in commercial diesel truck transport and other related applications

Approach

- Propose initial kinetic network for individual model compounds
- Develop intuitive kinetic models for individual model compounds
- Conduct combinatorial fuel compound studies
- Develop surface response maps for binary fuel mixtures
- Correlate fuel reforming rates (versus process conditions) and catalyst type for individual and combined diesel constituents (surrogate diesel fuel)

Accomplishments

- Conducted combinatorial fuel compound studies
- Developed surface response maps for steam reforming (SR), partial oxidation (POX) and autothermal reforming (ATR) over Pt catalysts for single-component fuels
- Proposed probable kinetic schemes for different hydrocarbons

Future Directions

- Conduct ternary fuel compound studies
- Evaluate other fuel compounds within a classification to examine if similar reforming behavior exists
- Develop intuitive kinetic models for individual model compounds and benchmark fuel for particular catalyst types
- Continue evaluation of carbon formation
- Collaborate with Las Alamos National Laboratory to provide carbon deactivation kinetics
- Obtain experimental reactor performance data to validate reaction models and provide for fuel reactant mixing modeling capability suitable for CFD modeling codes
- Develop a detailed kinetic model that incorporates CFD

Introduction

The fuel processor is a critical component of fuel cell systems. The processor must be able to provide a clean, tailored synthesis gas to the fuel cell stack for long-term operation. Key characteristics desired for the processor (and the system) include low cost, high efficiency, maximum thermal integration, low maintenance intervals, and acceptable startup and transient response. There are several barrier issues that must be overcome to achieve these characteristics. Carbon formation, particularly upon

startup, must be minimized to avoid coking of the catalysts in the reformer and downstream fuel cell. Fuels containing sulfur can poison both the reforming catalysts and the fuel cell anode. High thermal mass components (some of which may have heat-ramp restrictions) can limit startup times and transient response. And finally, cost targets must be achieved to ensure commercial success.

Fundamental understanding for design and operation of reformers is important for successful technology development. One of the most fundamental engineering design parameters that can be measured in the laboratory is the intrinsic kinetics of a catalyst system. Once established for a particular feedstock and catalyst system, kinetics can be coupled with computational fluid dynamics (CFD) code to effectively design, optimize, and minimize hydrocarbon slip in autothermal reformer systems. In principle, the kinetics of NO_x formation, sulfur poisoning, carbon formation and catalyst aging can be added to allow for a complete predictive model for reformer performance and operation.

However, modeling of reforming systems is extremely complicated. Diesel fuel consists of a complex, variable mixture of hundreds of hydrocarbon compounds, containing mainly olefins, saturates and aromatics. Empirical expressions for space velocity or simple power law-type models are typically used to design reformers. Unfortunately, these tend to be limited to a specific catalyst, fuel composition, and operating point. Therefore, the development of validated predictive models that can account for variations in these parameters is necessary.

For the autothermal reforming of diesel with steam and oxygen, a complex reaction network is expected. Elucidation of this network and the development of a generalized complex network model for platinum catalysts will be the initial focus of this body of work. The overall kinetic approach employed will balance the level of detail that can accurately be accommodated by CFD code with the ability to easily update kinetic parameters for a new catalyst system.

Approach

To select an appropriate model, it is necessary to understand the reaction mechanisms and pathways for the chemical system. One approach to gaining that understanding is surface response mapping. This is a statistical technique used to map characteristic responses (e.g. yield, conversion, carbon buildup, etc.) to input variables (O_2/C, H_2O/C, temperature, space velocity, etc.) over a defined region. It identifies the significance of parameters and their interactions. Also, it provides data that can lead to validation of kinetic models and can test the statistical significance of proposed reaction pathways. As the most important mechanisms and reaction pathways are defined, appropriate models will be selected. Kinetic measurements of binary components or individual reaction systems will be developed and used to validate the model. This will initially be done for a platinum catalyst and extended to other catalyst systems as needed to complete the model.

A fixed bed reactor system was used to conduct the experiments. The reactor was operated continuously at steady state. γ-Alumina-supported platinum (0.611 wt%) catalyst (surface area 103 m^2/g) was used in this study as a base catalyst. A summary of reaction conditions is given in Table 1.

Table 1. Experimental Conditions

	ATR	SR	POX
O_2/C	0.3	0.0	0.5
H_2O/C	1.5	3.0	0.0
T (°C)	750 - 850	750 - 850	750 - 850
GHSV (h^{-1})	50,000 - 150,000 20,000 - 65,000*	50,000 - 150,000 20,000 - 65,000*	50,000 - 150,000 20,000 - 65,000*
*If 1-methylnaphthelene is in feed			

A mixture of two model compounds from different hydrocarbon classes, e.g. one from aromatics and one from paraffins, will be used to understand the combinatorial effects of feed components. Tetradecane, decalin, and 1-methyl-naphthalene are identified as model

compounds to represent paraffins, naphthenes, and aromatics, respectively, found in diesel. A rotatable-central-composite design will be used for process optimization. Each combination of model compounds representing two different organic classes in diesel will undergo autothermal, partial oxidation, and steam reforming at the temperature and space velocity range given in Table 1.

A gas chromatography technique was used to identify and separate the reaction products. The gases (N_2, O_2, CO, CO_2, and CH_4) were analyzed using a thermal conductivity detector (TCD), and the gaseous hydrocarbons were analyzed using a flame ionization detector (FID). Gas chromatography (Perkin Elmer's AutoSystem XL) coupled with mass spectrometry (Perkin Elmer's TurboMass Gold) was used to quantify and identify the complex liquid hydrocarbon product mixture that formed at various hydrocarbon conversions. Product yield is reported as a percentage of the theoretical yield based on moles of carbon in hydrocarbon fed to the reactor. For example, the yield of product A (H_2, CO, and CO_2) can be defined as

$$\text{Yield of A (\%)} = \frac{\text{Moles of A produced}}{N \times \text{moles of hydrocarbon fed to the reactor}} * 100$$

where N is the number of carbons in hydrocarbon fuel used in this study. In some cases, H_2 yields may be higher than 100% since steam reforming and water gas shift reaction also contribute in H_2 production apart from hydrocarbons.

Results

Statistical Analysis of Reforming Process

The yields of individual species from hydrocarbon reforming, which depend on the space velocity and reaction temperature, can be described by the equation

$$z = b_0 + b_1 x + b_2 y + b_{11} x^2 + b_{22} y^2 + b_{12} xy \qquad (1)$$

where z is the yield of individual species after completion of the reaction, x is temperature (K), y is gas hourly space velocity (GHSV)(hr^{-1}), and b_0....b_{22} are the coefficients of the model. The coefficients of Equation 1 were estimated by making use of the responses of experiments for the standardized values of x and y which varied in the range given in Table 1. Relationships between yield (z) and two quantitative variables x (space velocity) and y (reaction temperature) are represented by response surface curves as shown in Figures 1-5. Coefficients of quadratic Equation 1 are summarized in Table 2 for H_2 and CO yields from autothermal reforming of various types of raw materials used in this study. Quadratic fit of data from response surface mapping was excellent (>90%).

Different hypothetical reaction schemes of the process are established based on the response surface methodology studies. Each of the proposed kinetic schemes is being evaluated with respect to the experimental results using an iterative predictor-corrector method based on the Himmelblau-Jones-Bischoff technique [2, 3]. The following criteria are

Table 2. Coefficients of Quadratic Equations for Autothermal Reforming of Model Components

Fuel	X	Coefficients						R^2
		b_0	b_1	b_2	b_{11}	b_{22}	b_{12}	
Tetradecane + Decalin	H_2	-2205.8	3.97	$6.7e^{-4}$	$-1.8e^{-3}$	$-5.3e^{-10}$	$-6.8e^{-7}$	92.2
	CO	-838.5	1.56	$-9.5e^{-4}$	$-7.0e^{-4}$	$-2.2e^{-9}$	$1.1e^{-6}$	95.6
1-Methylnaphthalene + Decalin	H_2	-3237.1	5.62	$3.1e^{-3}$	$-2.4e^{-3}$	$1.9e^{-10}$	$-3.3e^{-6}$	98.0
	CO	-1953.6	3.44	$1.1e^{-3}$	$-1.5e^{-3}$	$-1.2e^{-9}$	$-9.3e^{-7}$	94.9
Tetradecane + 1-Methylnaphthalene	H_2	-4678.5	9.12	$-5.7e^{-3}$	$-4.4e^{-3}$	$8.3e^{-9}$	$4.4e^{-6}$	95.0
	CO	17.95	-0.028	$-2.3e^{-3}$	$3.7e^{-5}$	$6.9e^{-10}$	$2.0e^{-6}$	93.0

being utilized to assess the validity of the model: calculated rate constants (positive values and follow Arrhenius Law), minimized value of objective function, and calculated profile of species concentration variations.

Earlier in this project, individual model compounds representing each homologous series present in diesel were evaluated to understand their reforming properties over Pt catalysts [1]. It was noted that each model compound behaved differently kinetically upon reforming under similar conditions. The hydrogen production rates at the same conditions were observed in this order: Aromatics << Naphthenes < Paraffins. Hydrocarbon product distributions depended greatly on the model compound, type of reforming performed, and the process parameters (space velocity and reaction temperature).

This year, we conducted binary fuel compound studies to understand the combinatorial effects of feed components. Therefore, surface response maps were developed for steam reforming, partial oxidation and autothermal reforming over Pt catalysts for three binary fuel mixtures (n-tetradecane + 1-methylnaphthalene, decalin + 1-methylnaphthalene, and n-tetradecane + decalin).

Figures 1-3 show the effect of temperature and space velocity on the yields of H_2, CO, and CO_2 from the autothermal reforming of 1-methylnaphthalene (aromatic) + n-tetradecane (paraffin). Figures 4-5 show the yields of H_2 from the autothermal reforming of 1-methylnaphthalene + decalin (naphthene) and n-tetradecane + decalin, respectively. Generally, the yields of H_2 and CO increase with increasing reaction temperature and decreasing space velocity. However, the yields of CO_2 from autothermal reforming decrease with increasing temperature because the lower temperatures favor the water-gas-shift reaction, while the reverse of the water-gas-shift reaction is facilitated at higher temperatures.

Difference in the relative reactivity of components in a binary mixture as well as the type of reforming performed play important roles in the reforming of a binary mixture representing a diesel fuel to produce syngas. Overall yields from a binary
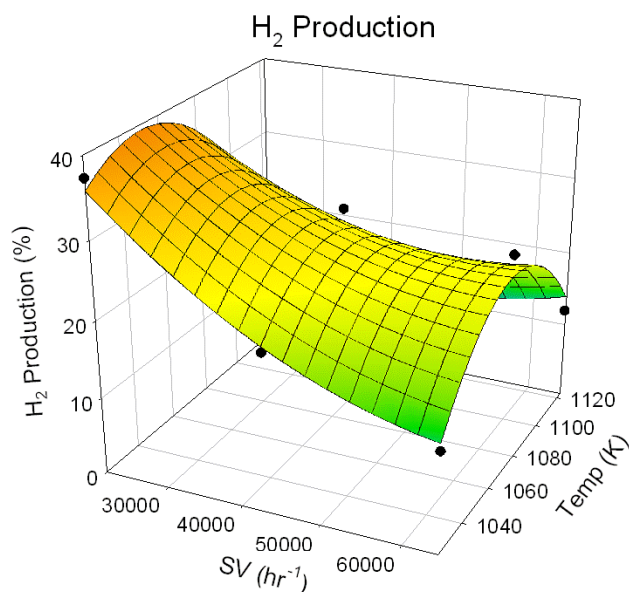

Figure 1. Yield of H_2 from ATR of n-tetradecane + 1-methylnaphthalene (O_2/C = 0.3 and S/C = 1.5)
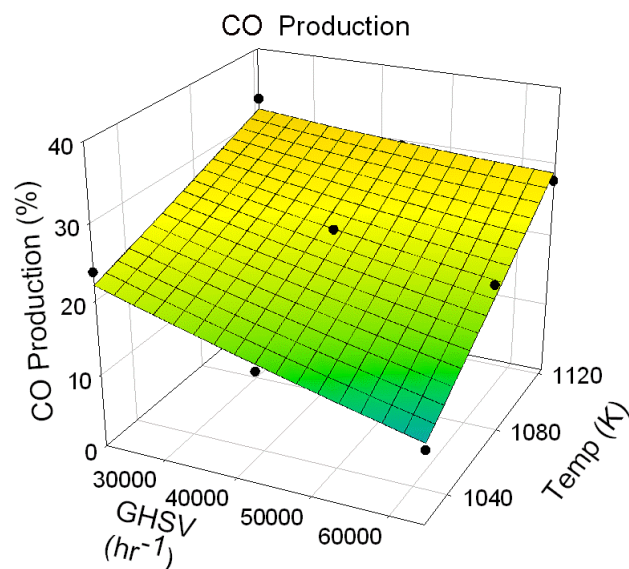

Figure 2. Yield of CO from ATR of n-tetradecane + 1-methylnaphthalene (O_2/C = 0.3 and S/C = 1.5)

diesel mixture are not simply the sum of yields from individual fuel components. Relative reactivity of one fuel component considerably affects the conversion pattern of others as well as the overall product distribution. Larger effects on reforming are noticed for greater differences in reactivity of binary components. For example, aromatics are relatively less reactive compared to paraffins; hence, the
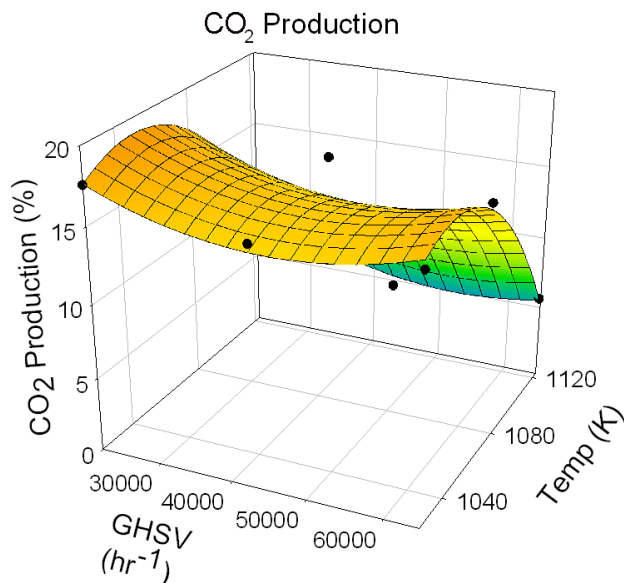
CO$_2$ Production

Figure 3. Yield of CO_2 from ATR of n-tetradecane + 1-methylnaphthalene ($O_2/C = 0.3$ and $S/C = 1.5$)
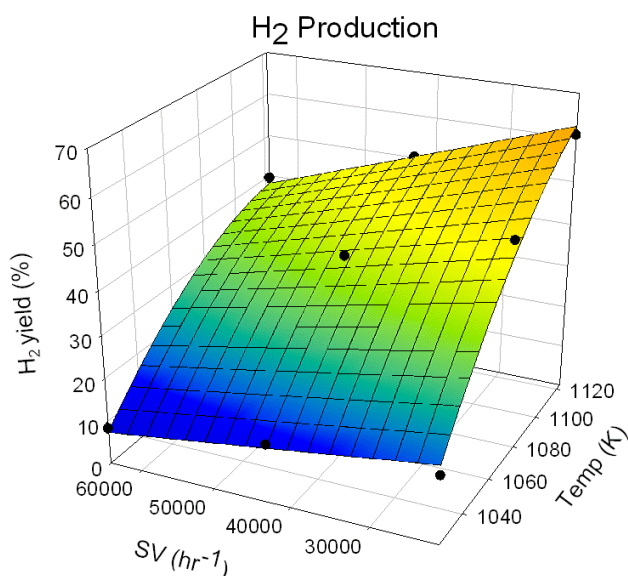
H$_2$ Production

Figure 4. Yield of H_2 from ATR of 1-methylnaphthalene + decalin ($O_2/C = 0.3$ and $S/C = 1.5$)

highly reactive paraffins would consume available O_2 in POX and ATR reactions. Therefore, conversion of highly reactive fuel components proceeds towards completion and produces
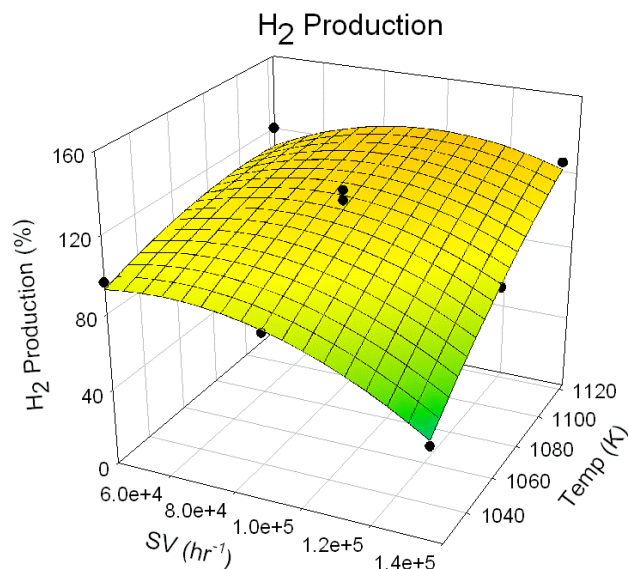
H$_2$ Production

Figure 5. Yield of H_2 from ATR of n-tetradecane + decalin ($O_2/C = 0.3$ and $S/C = 1.5$)

combustion products, while not enough O_2 is spared for the less reactive component. Consequently, the less reactive component is predominantly subjected to pyrolysis reaction.

Partial oxidation reforming was affected significantly by the difference in the reactivity of fuel components, while steam reforming was not affected much from the difference in reactivity of fuel components since water was present in abundance in steam reforming. Autothermal reforming was somewhere in the middle.

Side reactions specific to one component play an important role in the reforming of a mixture. For example, aromatics are more prone to coking upon reforming; therefore, the presence of aromatics in the mixture can lower the yields of syngas over time due to catalyst deactivation. Also, the catalyst surface-component interaction may play an important role in the reforming of a mixture. For example, aromatics have an abundance of pi-electrons, so they may occupy catalyst active sites for longer time due to pi-complexation between d-orbitals in the metal and pi-electrons. Hence, there won't be enough reactive sites available for the desired reaction to occur.

Conclusions

- Overall yields are not the sum of yields from individual fuel components.
- Relative reactivity of one fuel component considerably affects the conversion pattern of others.
- The greater the difference in relative reactivity, the larger the effect.
- Conversion of highly reactive fuel components proceeds towards completion.
- Reverse of water gas shift reaction dominates at high temperatures.
- Partial oxidation reforming is affected significantly by the difference in reactivity of fuel components.
- Highly reactive components consume available O_2, produce combustion products.
- O_2 not spared for the less reactive component, pyrolysis reaction dominates.
- Steam reforming not affected much by the difference in reactivity of fuel components.

References

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